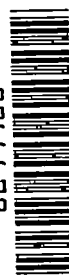


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TECHNICAL NOTE 3558

HEAT CAPACITY LAG OF GASEOUS MIXTURES

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and Sam Legvold

Iowa State College



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SUMMARY

The relaxation times for the excitation of molecular vibrations in a number of heavy gases have been measured with an acoustic interferometer. All the gases studied were found to have a single relaxation time, indicating that intermodal coupling in these gases is strong.

Only binary collisions are found to be important in the excitation of vibrations. The probability, in a given collision, of exciting or deexciting molecular vibrations in the halogen-substituted methanes appears to depend upon the relative energy of approach of the colliding molecules rather than upon the relative velocity.

The excitation of vibrations in polyatomic gases may well involve the formation of a complex molecule with a very short life.

INTRODUCTION

About 30 years ago, investigators in the field of ultrasonics discovered that the velocity of sound in polyatomic gases is a function of the sonic frequency. This phenomenon is known as the dispersion of sound and may be explained by the failure of the translational, rotational, and vibrational energies of gas molecules to maintain thermal equilibrium with each other at high acoustic frequencies. An irregularly high acoustic absorption accompanies this dispersion in acoustic velocity.

Numerous investigators have measured the dispersion of sound caused by the lagging of the vibrational energy (also referred to as the thermal relaxation process). Nearly all the investigations have been made in diatomic and triatomic gases in which the vibrational relaxation time is relatively long and the region of dispersion is at easily attainable frequencies. Advances in electronics have recently made possible the accurate measurement of acoustic velocities at very high frequencies. Considerable interest has been aroused in the study of dispersion due to the lag of rotational and translational energies; study of the vibrational energy lag in heavy organic gases, which also necessitates high-frequency measurements, has been neglected. It is the purpose of this paper to

report some measurements of sonic dispersion made in heavy gases and to attempt clarification of certain fundamental properties of the vibrational excitation process in these gases.

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SYMBOLS

A, A_0, a	} Beattie-Bridgman gas constants
B, B_0, b	
C_{atomic}	contribution to C_v made by atomic excitation
C_0	molar heat capacity at constant volume at frequencies below dispersive region
C_{rot}	contribution to C_v made by molecular rotations
C_{trans}	contribution to C_v made by molecular translational motion
C_v	molar heat capacity at constant volume
C_{vib}	contribution to C_v made by molecular vibrations
C_ω	effective C_v at angular frequency ω in dispersive region
C_∞	molar heat capacity at constant volume at frequencies above dispersive region
c	velocity of light
f	sonic frequency
f_{inf}	sonic frequency at which inflection point of dispersion curve occurs
h	Planck's constant
k	Boltzmann's constant

M	molecular weight
N	average number of collisions experienced by a molecule per second
n	ratio of ϵ^* to $h\nu_1$
\bar{n}	number of molecules of gas per unit volume
n_0	number of molecules per unit volume whose vibrations are in ground state
n_1	number of molecules per unit volume whose vibrations are in first excited state
P_{10}	average of p_{10} over proper velocity or energy distribution
p	pressure
p_{10}	probability that a molecule in first excited vibrational state will be deexcited by a collision; a function of velocity or energy of approach
R	universal gas constant
s	range of intermolecular forces
T	temperature, $^{\circ}\text{K}$
t	time, sec
V	velocity of sound
V_{bb}	velocity of sound in a Beattie-Bridgman gas
V_{ideal}	velocity of sound in an ideal gas
V_0	velocity of sound at frequencies below dispersive region
V_{∞}	velocity of sound at frequencies above dispersive region
v	relative velocity of two colliding molecules
Z_{10}	average collision lifetime of first excited state; average number of collisions necessary to deexcite a molecule in first excited state

α	steric factor; probability that a collision will take place with molecules favorably oriented for excitation
ϵ	relative approach energy of two molecules
ϵ^*	minimum value of ϵ required for vibrational excitation
θ	vibrational relaxation time
μ	reduced molecular weight of two colliding molecules
ν	vibrational frequency per second
$\bar{\nu}$	wave number per centimeter, ν/c
ν_1	vibrational frequency per second of lowest mode
ξ	velocity correction due to absorption
ρ	density, g/liter
$\bar{\rho}$	density, moles/liter, ρ/M
σ	see equation (27)
ω	angular frequency of sound, $2\pi f$
$\omega_{\text{inf}} = 2\pi f_{\text{inf}}$	

THEORY OF ACOUSTIC DISPERSION

Propagation of Sound

Richards (ref. 1, 1939) has derived an expression for the velocity of sound in an isotropic homogeneous medium:

$$v^2 = \left(\frac{\partial p}{\partial \rho} \right)_T + \left(\frac{\partial p}{\partial T} \right)_\rho^2 \frac{MT}{\rho^2 C_v} \quad (1)$$

in which p is the pressure; T , the temperature; C_v , the molar heat capacity at constant volume; ρ , the density; and M , the molecular weight. For the velocity in an ideal gas, the derivatives may be evaluated from the ideal-gas equation $p = \frac{RT}{V} = \frac{RT\rho}{M}$ and substituted into equation (1):

$$V_{\text{ideal}}^2 = \frac{RT}{M} \left(1 + \frac{R}{C_v} \right) \quad (2)$$

An equation of state frequently applied to polyatomic molecules is that of Beattie and Bridgman:

$$p = \frac{RT(v + B)}{v^2} - \frac{A}{v^2} \quad (3)$$

where

$$A = \left(1 - \frac{a}{v} \right) A_0$$

$$B = \left(1 - \frac{b}{v} \right) B_0$$

a , b , A_0 , and B_0 being constants characteristic of the given gas.

This equation may also be written in terms of $\bar{p} = \frac{p}{M}$:

$$p = RT\bar{p} + (RTB_0 - A_0)\bar{p}^2 + (A_0a - RTB_0b)\bar{p}^3 + \dots \quad (4)$$

Substitution of equation (4) into equation (1) produces an expression for the square of the velocity in a Beattie-Bridgman gas:

$$V_{\text{bb}}^2 = \frac{1}{M} \left[RT + 2\bar{p}(RTB_0 - A_0) + 3\bar{p}^2(A_0a - RTB_0b) \right] + \frac{R^2T}{MC_v} \left[1 + 2\bar{p}B_0 + \bar{p}^2(B_0^2 - 2B_0b) \right] \quad (5)$$

Terms in \bar{p}^3 and higher have been omitted. Note that as \bar{p} becomes very small (low pressures) equation (5) reduces to equation (2).

In any gas molecule, the specific heat at constant volume may be expressed in terms representing contributions from translatory motion, internal vibrations and rotations, and atomic excitation:

$$C_v = C_{\text{trans}} + C_{\text{vib}} + C_{\text{rot}} + C_{\text{atomic}} \quad (6)$$

The value of each quantity depends upon temperature, and, according to the equipartition theorem of energy, in a body at equilibrium the energy (and therefore the heat capacity) must be distributed among these terms in a definite manner. At room temperatures most atoms are in their ground state and C_{atomic} is negligible. If the equilibrium between these types of internal energy is disturbed, each mode again approaches its equilibrium value at a rate characterized by its own relaxation time. Vibrational relaxation times cover the range 10^{-2} to 10^{-10} second.

As long as thermal disturbances occur slowly, C is correctly given by equation (6). Since the period of a disturbance is so shortened as to be of the order of one of these relaxation times (as happens when a sound wave of high frequency is incident), the equilibrium process is unable to follow the rapid thermal cycle, and the net effect is that a part of the heat capacity drops out completely. Thus C_v and V^2 depend upon frequency throughout the dispersive region.

If C_0 denotes the heat capacity at constant volume below the dispersive region and C_∞ , the heat capacity above this region, then

$$C_\infty = C_{\text{trans}} + C_{\text{rot}} \quad (7)$$

and

$$C_0 = C_\infty + C_{\text{vib}} \quad (8)$$

Following the technique of Richards (ref. 1, 1939), the heat capacity at acoustic angular frequency ω within the dispersive region may be written

$$C_\omega = C_\infty + \frac{C_0 - C_\infty}{1 + i\omega\theta} \quad (9)$$

where θ is the appropriate relaxation time and ω is 2π times the acoustic frequency f . Substitution of equations (7) and (8) into equation (2) yields

$$V_\infty^2 = \frac{RT}{M} \left(1 + \frac{R}{C_\infty} \right) \quad (10)$$

$$V_0^2 = \frac{RT}{M} \left(1 + \frac{R}{C_0} \right) \quad (11)$$

Similarly, substitution of equation (9) into equation (2) will yield a complex expression, the real part of which represents the phase velocity of sound at frequencies within the dispersive region:

$$V_{\text{ideal}}^2 = \frac{RT}{M} \left(1 + R \frac{C_0 + \omega^2 \theta^2 C_\infty}{C_0^2 + \omega^2 \theta^2 C_\infty^2} \right) \quad (12)$$

The inflection point of equation (12) may be found by differentiation:

$$\omega_{\text{inf}} = \frac{C_0}{\theta C_\infty} \quad (13)$$

Similarly, substitution of equation (9) into equation (5) gives an expression for the square of the velocity in a Beattie-Bridgman gas:

$$V_{\text{bb}}^2 = \frac{1}{M} \left[RT + 2\bar{p}(RTB_0 - A_0) + 3\bar{p}^2(A_0a - RTB_0b) \right] + \frac{R^2 T}{M} \left[1 + 2\bar{p}B_0 + \bar{p}^2(B_0^2 - 2B_0b) \right] \left(\frac{C_0 + \omega^2 \theta^2 C_\infty}{C_0^2 + \omega^2 \theta^2 C_\infty^2} \right) \quad (14)$$

The dispersion curve for an ideal gas, plotted from equation (12), is shown in figure 1.

Multiple Dispersion

Thus far it has been assumed that for a given gas the relaxation process may be characterized by a single relaxation time θ . This is equivalent to assuming that all modes of vibration are excited with the same relaxation time and, furthermore, that all vibrational transitions occur with the same relaxation time as transitions from the ground state to the first excited state. That all transitions between the states of a given mode of vibration have the same relaxation time has been shown by Landau and Teller (ref. 2, 1936). If, however, the couplings between different modes of vibration were so weak that they must be excited independently by collisions and therefore possess different relaxation times, a step-shaped velocity-dispersion curve would result.

Some evidence favoring the existence of multiple dispersive regions has been reported. Pielemeier (ref. 3, 1943) and Buschmann and Schäfer (ref. 4, 1941) have reported a possible second step on the velocity-dispersion curve of carbon dioxide. Alexander and Lambert (ref. 5, 1942)

found three dispersive regions in acetaldehyde. A later article by Lambert and Rowlinson (ref. 6, 1950), however, points out that the multiple dispersions of velocity are due to errors in calculation resulting from an ungrounded assumption that dimerization equilibrium does not keep pace with the acoustic cycle.

Great difficulty would be experienced in the observation of multiple dispersive regions in triatomic molecules, if indeed such exist. At room temperature one mode usually accounts for most of the vibrational contribution to specific heat. Any steps on the velocity-dispersion curve due to the other modes would be so small that they would be difficult to detect. Detection of multiple dispersion due to a lack of intermodal coupling, if it exists, might be most probable in molecules such as the halogen-substituted methanes since these have modes of low frequency which can be excited at room temperatures. On the other hand, if intermodal coupling is strong enough so that energy is transferred readily from one mode to another, only a single relaxation time will be observed. Presumably this will be the relaxation time for the mode of lowest frequency.

Trace Catalyst Effect

A phenomenon which has been observed in relaxation-time studies is the "trace catalyst" effect. Collisions between unlike molecules are sometimes much more efficient in the excitation of vibrations than those between like molecules. Eucken and Becker (ref. 7, 1934) observed that in a collision between two molecules which have a chemical affinity for each other the probability of vibrational excitation is large. Landau and Teller (ref. 2, 1936) suggested that excitation is more probable when the two colliding molecules approach each other at a high velocity, thus explaining the effectiveness of hydrogen and helium as catalysts. Several important catalytic gases are discussed by Walker (ref. 8, 1951).

Multiple Collisions

In general, a certain average number of collisions are required to excite or deexcite the molecular vibrations in a given gas. Since the number of binary collisions is proportional to the pressure of the gas, it follows that the relaxation time will be inversely proportional to the pressure when binary collisions are responsible for vibrational excitation. If triple collisions are primarily responsible, the relaxation time will be inversely proportional to the square of the pressure.

In equations such as expressions (12) and (14) dealing with acoustic dispersion, the independent variable is always $\omega\theta$ rather than ω . Hence, if the relaxation time θ is inversely proportional to the

pressure, the dispersion curve may well be drawn with $\log f/p$ as the abscissa instead of $\log f$. This is a great advantage in experimental work, since it provides a method of obtaining a continuous range of frequencies without changing the frequency of the sound source. Of course, it must first be ascertained which type of collision is responsible for vibrational excitation so that the correct pressure dependence is used.

No conclusive evidence has been presented supporting any importance of collisions of orders above the second. Walker (ref. 8, 1951) suggested that certain data of previous investigators, involving carbon oxysulfide with added quantities of helium and argon, might be interpreted on the basis that triple collisions are of greater importance than the binary type. Walker, Rossing, and Legvold (ref. 9, 1954) later reported that triple collisions are not important in the excitation by helium, argon, and nitrogen of nitrous oxide, which is very similar in structure to carbon oxysulfide.

THEORY OF VIBRATIONAL EXCITATION BY COLLISIONS

Relaxation Theory

A gas will be considered which has n_1 molecules with vibrations in the first excited state and n_0 molecules in the ground state per unit volume. If at all times $n_0 - n_1 = \bar{n}$, a constant, the continuous exchange of molecules between states 0 and 1 may be characterized by the equation

$$\frac{dn_1}{dt} = f_{01}n_0 - f_{10}n_1 \quad (15)$$

in which f_{01} specifies the number of $0 \rightarrow 1$ transitions per ground state molecule per second and f_{10} , the corresponding number of $1 \rightarrow 0$ transitions per excited molecule.

When the gas is in equilibrium, $\frac{dn_1}{dt} = 0$ and, therefore, according to the principle of detailed balancing, the total number of transitions in each direction are equal. At equilibrium

$$n_1 = n_0 e^{-h\nu/kT} \quad (16)$$

and so

$$f_{01} = f_{10} e^{-h\nu/kT} \quad (17)$$

In the above equations h and k are the Planck and Boltzmann constants, respectively, ν is the frequency of molecular vibrations, and T is the temperature in $^{\circ}\text{K}$.

Since $\bar{n} = n_0 + n_1$ at all times, equation (15) may be written:

$$\frac{dn_1}{dt} + n_1(f_{01} + f_{10}) = f_{01}\bar{n} \quad (18)$$

Since \bar{n} is constant, the solution to this differential equation for nonequilibrium is

$$n_1 = c_1 + c_2 e^{-(f_{01}+f_{10})t} \quad (19)$$

where c_1 and c_2 are constants. The relaxation time of this process can then be seen to be

$$\theta = \frac{1}{f_{01} + f_{10}} \quad (20)$$

Here θ is the time necessary for the departure from thermal equilibrium to be reduced to $1/e$ of its initial value. Some authors assume that $h\nu/kT \gg 1$ and $f_{01} \ll f_{10}$ and, hence, that $\theta \approx 1/f_{10}$. At vibrational frequencies less than about $\nu = 1.5 \times 10^{13}$ second $^{-1}$ (corresponding to $\bar{\nu} = 500$ centimeter $^{-1}$ in spectroscopic wave numbers, since $\bar{\nu} = \nu/c$), this assumption is ungrounded.

If the average number of collisions which a molecule makes per second is denoted by N , f_{01} and f_{10} may be written in terms of P_{01} and P_{10} , the probabilities that a molecule in the ground or first excited state will be excited or deexcited, respectively, in a collision. Then,

$$\left. \begin{aligned} f_{01} &= P_{01}N \\ f_{10} &= P_{10}N \end{aligned} \right\} \quad (21)$$

The reciprocals of P_{01} and P_{10} , Z_{01} and Z_{10} , will give the mean collision lifetimes of the ground and the first excited states, respectively. Substitution of equations (17) and (21) into equation (20) produces

$$\begin{aligned}\theta &= \frac{1}{NP_{10}(1 + e^{-h\nu/kT})} \\ &= \frac{1}{NP_{01}(1 + e^{h\nu/kT})}\end{aligned}\quad (22)$$

Therefore:

$$\frac{Z_{01}}{Z_{10}} = \frac{1 + e^{h\nu/kT}}{1 + e^{-h\nu/kT}} \quad (23)$$

or

$$Z_{01} = Z_{10}e^{h\nu/kT} \quad (24)$$

In case $h\nu \ll kT$ (not realizable at ordinary temperatures)

$$Z_{01} \approx Z_{10} \quad (25)$$

Prediction of P_{10}

Landau and Teller (ref. 2, 1936) have developed a theory which has been very successful in explaining energy-transfer probabilities in relatively simple molecules. They write an expression for the probability of deexcitation of a vibrating molecule p_{10} in a single collision when the relative velocity of approach of the molecules lies within the range v to $v + dv$:

$$p_{10} = \alpha e^{-2\pi v s / v} \quad (26)$$

where α is a steric factor which gives the probability that a collision will find the molecules favorably oriented for excitation or deexcitation,

s is the range of intermolecular forces, and ν , the vibrational frequency. Bethe and Teller (ref. 10, 1942) integrate the above expression over a Maxwellian distribution of velocities to obtain

$$P_{10} = C\sigma e^{-\sigma} \quad (27)$$

where

$$\sigma = 0.090(\bar{\nu}s)^{2/3} \left(\frac{\mu}{T}\right)^{1/3}$$

$$C = \left(\frac{4}{3}\right)^{3/2} \alpha$$

μ is the reduced molecular weight of the colliding molecules, $\bar{\nu}$ is the vibrational frequency in centimeter⁻¹, measured in units of 10⁻⁹ centimeter, and T is in °K.

Recent theory by Schwartz, Slawsky, and Herzfeld (ref. 11, 1952), based on the approach of Zener, makes use of an exponential repulsion and a one-dimensional model. These authors arrive at a somewhat more complicated expression for P_{10} which, they point out, has essentially the same dependence upon μ , $\bar{\nu}$, and T as the theory of Landau and Teller.

Fogg, Hanks, and Lambert (ref. 12, 1953) have measured the vibrational relaxation times of several halomethane vapors and have calculated the number of collisions necessary to excite the lowest modes of vibration. At least four of these gases appear to fit an empirical relation of the form $P_{01} = e^{-X\nu_1}$ in which ν_1 is the frequency of the lowest vibrational mode and X is a proportionality constant characteristic of the particular group of gases. This suggests that the probability of vibrational excitation depends upon the energy of approach of the colliding molecules rather than upon the velocity of approach. An energy excitation theory, based on the above suggestion, will now be further developed by examination of the deactivation process.

It may be assumed that the probability p_{10} of deexciting a vibrating molecule in a given collision can be written in terms of the relative energy of approach ϵ of the colliding molecules:

$$P_{10} = \left. \begin{aligned} &= \alpha && \epsilon \geq \epsilon^* \\ &= 0 && \epsilon < \epsilon^* \end{aligned} \right\} \quad (28)$$

In equation (28), α is the steric factor and ϵ^* is some minimum relative energy of approach which must be exceeded in order to produce deexcitation. If it is assumed that the mode of lowest frequency ν_1 is the first to be deexcited, ϵ^* may be written $\epsilon^* = nh\nu_1$ where n is some constant.

Integration of equation (28) from $\epsilon = \epsilon^*$ to $\epsilon = \infty$ gives the probability of deexcitation in a single collision:

$$\begin{aligned} P_{10} &= \alpha e^{-\epsilon^*/kT} \left(\frac{\epsilon^*}{kT} + 1 \right) \\ &= \alpha e^{-nh\nu_1/kT} \left(\frac{nh\nu_1}{kT} + 1 \right) \end{aligned} \quad (29)$$

The corresponding probability for excitation may be written:

$$P_{01} = \alpha e^{-(n+1)h\nu_1/kT} \left(\frac{nh\nu_1}{kT} + 1 \right) \quad (30)$$

The above relations picture vibrational excitation and deexcitation as involved processes requiring a certain minimum energy of approach. It is tempting to assume that vibrational excitation and deexcitation take place only when a molecule is able to penetrate very deeply into the force field of another, the penetration requiring a certain amount of energy. It is even possible that the collision partners form a compound molecule with a very short life, during which energy may pass readily between translational and vibrational degrees of freedom. The process of formation of the compound molecule would require a certain minimum amount of energy. It should be noted that the probabilities for the excitation and deexcitation processes differ by a factor $e^{-h\nu_1/kT}$. Fogg, Hanks, and Lambert (ref. 12, 1953) have apparently treated them as being the same.

Trace catalysts may still exist for gases which obey the energy excitation theory, but gases which catalyze diatomic and triatomic gases may not produce the same result in polyatomic gases. Hydrogen and helium apparently are strong catalysts in diatomic and triatomic gases because they have a very high velocity at ordinary temperatures. To be a catalyst in a gas obeying the energy excitation theory, however, a

gas must be able to penetrate the force field of another easily, or to form a compound molecule readily, and have a fairly large steric factor.

Heat Capacities of Gases

According to equation (6), the heat capacity of a gas is made up of contributions from molecular vibrations, rotations, and translations. At sufficiently high temperatures, each degree of translation or rotation contributes $\frac{1}{2}R$, and each vibrational mode contributes R times the degree of degeneracy.

At room temperatures, C_{rot} is fully developed in polyatomic gases. Thus the rotational contribution from linear polyatomic molecules is R , and the contribution from nonlinear polyatomic molecules is $\frac{3}{2}R$, since they have moments of inertia along three perpendicular directions. Translational energy, also characterized by three degrees of freedom, contributes $\frac{3}{2}R$.

Vibrational heat capacities, on the other hand, are rarely complete. Assuming that the molecules are perfect harmonic oscillators, the vibrational contribution to heat capacity may be written in terms of the frequencies of the n modes each having a degeneracy of order j :

$$C_{\text{vib}} = \sum_{i=1}^n \frac{j(h\nu_i/kT)^2 R}{2 [\cosh(h\nu_i/kT) - 1]} \quad (31)$$

Spectroscopic data indicate that molecular vibrations are not perfectly harmonic, and thus a transition from the second excited state to the first excited state does not produce the same frequency as that produced by a transition from the first state to the ground state. The error in V_0 introduced by the neglect of this anharmonicity in calculating C_{vib} is about 0.03 percent. The total heat capacity at constant volume, at room temperature and below the dispersive region in polyatomic molecules, may then be given as

$$C_0 = 3R + C_{\text{vib}} \quad (32)$$

where C_{vib} is calculated from equation (31). Above the dispersive region

$$C_{\infty} = 3R \quad (33)$$

EXPERIMENT

Apparatus

The velocity of sound has been measured by means of an interferometer of the Pierce type. A cross section of the acoustic chamber used to measure wavelengths is shown in figure 2. A gold-plated X-cut quartz crystal is clamped in its nodal plane and is driven near its frequency of resonance. An optically flat stainless-steel reflector is connected by a precision ground invar rod to a micrometer screw which has a least count of 0.001 millimeter. The crystal and the reflector are maintained parallel within 0.1 wavelength by means of three leveling screws.

The acoustic chamber is constructed from stainless steel, all seams being silver soldered. A copper gasket insures a vacuumtight seal. The invar rod, a mercury thermometer, and the oscillator leads pass through O-ring vacuum seals. The entire chamber is immersed in a constant-temperature water bath.

The crystal oscillator circuit is shown in figure 3. It is a variation of the Pierce type of circuit, using precision components throughout, and drives the crystal at a very constant frequency and amplitude. The theory of its design is discussed by Rossing (ref. 13, 1952). The frequency of the crystal is determined to a precision of 1 part in 10,000 by heterodyning the output of the oscillator with the signal from some convenient broadcast station to produce a beat note in the audiofrequency range. Most of the measurements were made with a 300-kilocycle crystal, although a 1,000-kilocycle crystal was sometimes employed.

Sharp peaks in the input impedance of the crystal indicate the positions of the reflector for which standing waves result. The circuit used to measure small changes in the crystal impedance is shown in figure 4. Voltages from the crystal are isolated by two cathode followers, independently rectified and fed into an unbalanced direct-current amplifier. A biased microammeter with five ranges measures the changes in the output of the direct-current amplifier. A General Electric vacuum thermocouple, which generates a voltage proportional to the amount of radiofrequency current through it, is used to measure the crystal current. The impedance-measuring circuit and the crystal oscillator receive their power from a stable power supply with an electronic voltage regulator of the degenerative feedback type. The power-supply circuit is shown in figure 5.

The gas-handling system is shown schematically in figure 6. A two-stage mechanical vacuum pump is capable of evacuating the entire system to a pressure of 0.2 micron. The pressure in the acoustic chamber is measured by a two-meter manometer and McLeod vacuum gage. A drying

chamber is available to remove traces of water-vapor impurity from gases; test gases can be drawn into a liquid-air cold trap and distilled into the chamber to remove traces of noncondensable gases. Kerotest packless diaphragm valves are used throughout the system. Before each measurement, the entire system is evaluated and outgassed to assure a gas sample of as high purity as possible.

Experimental Procedure

The velocity of sound was measured in each gas at a variety of f/p ratios by means of the acoustic interferometer. The corresponding values of V^2 were then plotted on semilogarithmic graphs in figures 7 to 20; V_{ideal}^2 was plotted using equation (12) with an arbitrary value of θ . This curve was then shifted along the f/p -axis until it best fit the experimental data, since according to equation (12) the effect of changing θ is merely to shift the entire curve along this axis. In those gases for which the dispersive region occurred at low frequencies and for which the Beattie-Bridgman constants were known, the V_{bb}^2 curve has been drawn using equation (14). The experimental values of V^2 were then corrected by adding the value of $V_{ideal}^2 - V_{bb}^2$ measured along the f/p ordinate corresponding to that point. Nearly all the values of V^2 are the result of 10 independent determinations of wavelength.

Since C_{rot} is fully developed in polyatomic gases at room temperatures, C_{∞} was calculated from equation (33); C_{vib} was then calculated using the vibrational wave numbers observed spectroscopically and equation (32); C_0 was then computed by equation (32). Thus the anharmonicity of the molecular vibrations was taken into account. Values of C_{vib} are given in table I; also given are values of C_1 , that part of C_{vib} contributed by the lowest vibrational mode.

The gases used in the experiment, which were of the highest purity available, were as follows: $CHClF_2$ (chlorodifluoromethane), $CHCl_2F$ (dichlorofluoromethane), CCl_2F_2 (dichlorodifluoromethane), CH_3Cl (chloromethane), CH_3Br (bromomethane), CCl_3F (trichlorofluoromethane), and $CClF_3$ (chlorotrifluoromethane), which were purchased from Matheson Co., Inc., and $CBrF_3$ (bromotrifluoromethane), CH_2ClF (chlorofluoromethane), CH_2F_2 (difluoromethane), CBr_2F_2 (dibromodifluoromethane), $CBrClF_2$ (bromochlorodifluoromethane), CF_4 (tetrafluoromethane), and CHF_3 (trifluoromethane), which were furnished by the Jackson Laboratory of E. I. du Pont de Nemours & Co., Inc. The purities reported by the suppliers of the gases are listed in table I. Several of the above gases

were stored in cylinders as gas over liquid. These gases were withdrawn in their liquid phase to minimize contamination by air and noncondensable gases. Others were liquified by use of the liquid-nitrogen cold trap and then evaporated into the system after pumping off all noncondensable vapor. The close fit of the low-frequency experimental data to the calculated values of V_0^2 demonstrates the high degree of purity of the gases used.

Values of f_{inf} were taken from the curves in figures 7 to 20. The corresponding values of θ were then calculated by use of equation (13). After the best fit was obtained with the experimental data, the theoretical dispersion curves were further moved along the f/p -axis to establish reasonable limits to the fit. From these limits the probable errors were calculated. Values of θ appear in table II.

Since it was observed that the dispersion curves gave no evidence of the existence of multiple relaxation times, it was assumed that the lowest vibrational mode was excited with its characteristic relaxation time and that the energy passed freely to the other modes. The relaxation time of the lowest mode θ_1 is given by the expression.

$$\theta_1 = \theta \frac{C_1}{C_{vib}} \quad (34)$$

in which C_1 is that part of C_{vib} corresponding to the lowest vibrational mode. Values of θ_1 were calculated from equation (34) and appear in table II.

Collision rates R were calculated from gas kinetic theory, using measured or calculated values of gas viscosity, and Z_{10} was calculated for each gas by means of equation (21), using for θ the relaxation time of the lowest mode θ_1 calculated from equation (34). These values of Z_{10} , together with corresponding values of R , also appear in table II.

Experimental Results

It may be noted in figures 7 through 20 that none of the gases measured showed multiple dispersive regions. This indicates that intermodal coupling is relatively strong in these molecules, and the assumption made by the use of equation (34) is justified.

Furthermore, since the use of f/p along the axis of abscissas yields the proper form of dispersion curve, the excitation and deexcitation of molecular vibrations must be brought about principally by binary collisions.

Following the result of Landau and Teller given by equation (27), Z_{10} has been plotted against $\bar{v}_1^{2/3} M^{1/3}$ in figure 21. A theoretical curve has been drawn to fit the data using $s = 0.25A$ and $\alpha = 0.5$. This value of s is about one-eighth the diameter of the colliding molecules and therefore is not reasonable. A similar curve drawn with $s = 1A$ will not fit the data regardless of the value of α used. Furthermore, the data do not appear to fit a single curve of the type drawn. It therefore appears that the theory of Landau and Teller does not fit the deexcitation of molecular vibrations in these gases.

In figure 22 Z_{10} has been plotted against \bar{v} in accordance with equation (29) and the energy-excitation theory. Curves have been drawn using the values $\alpha = 0.1$ and $n = 1.8, 1.5, 2.8$, and 3.8 . The value of n to be used apparently depends upon the number of hydrogen atoms replaced from the methane molecule. The quantity $nh\nu_1$ gives the minimum energy of approach necessary to excite or deexcite the vibrations of the molecule. This is presumably the energy necessary for the molecules to penetrate deeply into each other's force fields or to form a compound molecule as previously suggested.

Fogg, Hanks, and Lambert (ref. 12, 1953) have measured the relaxation times of some of the halogen-substituted methanes. Their values for Z_{10} were computed from their relaxation data by making the assumption that $h\nu_1 \gg kT$ and hence that $Z_{10} \approx N\theta_1$. At values of $\bar{v}_1 < 500 \text{ centimeter}^{-1}$, this is not true and leads to error in Z_{10} at low frequencies. In accordance with equation (21), the authors' values for Z_{10} have been multiplied by a factor $1 + e^{-h\nu_1/kT}$. The values of Z_{10} thus corrected are recorded in table III.

Since their data were taken at temperatures of about 373°K , the temperature correction predicted by equation (29) has been used to correct Z_{10} to 300°K ; these values are also recorded in table III. The corrections thus calculated, however, were invariably larger than the differences between these points and the calculated Z_{10} curves. The values of Z_{10} for 373°K and also the values predicted for 300°K are shown in figure 22.

Several other authors have measured relaxation times in some of the halogen-substituted methanes. Byers (ref. 14, 1943), Eucken and Aybar (ref. 15, 1940), and Petralia (ref. 16, 1952) have used acoustic interferometers to measure relaxation times; Griffith (ref. 17, 1950) and Huber and Kantrowitz (ref. 18, 1947) have made measurements using impact nozzles of the Kantrowitz type. Their data are also reported in table III, and the corresponding values of Z_{10} are plotted in figure 22. Where the

measurements were made at temperatures more than a few degrees removed from 300° K, the data are corrected to this temperature by use of equation (29).

The fact that use of equation (29) gives too large temperature corrections might suggest that the steric factor α is a function of temperature. It is reasonable to assume that α , being a geometrical probability, is dependent upon the speed at which the molecules are rotating, which in turn is a function of temperature. The period of a rotation of a typical molecule is 10^{-12} second, which is of the same order as the duration of a molecular collision.

CONCLUSIONS

Measurements were made of sound dispersion in a number of heavy gases. On the basis of the data reported, the following conclusions may be drawn:

1. Intermodal coupling is so strong in the halogen-substituted methanes that once the vibrational mode of lowest frequency is excited the energy passes readily into the other modes.
2. Only binary collisions are important in the excitation of vibrations in the halogen-substituted methanes within limits of observation.
3. The probability, in a given collision, of exciting or deexciting molecular vibrations in the halogen-substituted methanes appears to depend upon the relative energy of approach of the colliding molecules rather than upon their relative velocity as the Landau-Teller theory predicts. In particular, the probability of excitation or deexcitation is negligible unless the relative energy of approach ϵ exceeds $\epsilon^* = nh\nu_1$ where ϵ^* is the minimum value of ϵ required for vibrational excitation, n is characterized by the number of hydrogen atoms replaced, h is Planck's constant, and ν_1 is the lowest vibrational frequency.
4. The excitation of vibrations in polyatomic organic molecules may be a complex process involving the formation of a compound molecule with a very short lifetime.
5. The steric factor probably depends upon temperature through its dependence upon rotational velocity.

Iowa State College,
Ames, Iowa, August 31, 1954.

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TABLE I

MOLECULAR WEIGHTS AND HEAT CAPACITIES

Gas	Purity, percent	M	ν_1 , cm ⁻¹	C_1 , cal/mole °K	C_{vib} , cal/mole °K
CH ₃ Br	99.4	94.95	611	1.03	2.26
CHClF ₂	97	86.48	369	1.45	5.99
CH ₃ Cl	99.5	50.49	732	.78	1.84
CCl ₃ F	99.9	137.38	244	4.05	10.63
CBrClF ₂	99.9	165.38	200	1.85	10.24
CF ₄	----	88.01	437	2.93	6.91
CH ₂ F ₂	99.7	52.03	532	1.19	2.32
CH ₂ ClF	99.9	68.48	358	1.56	3.46
CClF ₃	99.0	104.47	356	3.16	8.16
CHCl ₂ F	99.0	102.93	274	1.72	6.76
CHF ₃	----	70.02	508	2.48	4.78
CCl ₂ F ₂	97	120.92	260	1.76	8.63
CBr ₂ F ₂	99.9	209.84	165	1.88	10.55
CBrF ₃	----	148.93	297	4.24	9.84

TABLE II

RELAXATION TIMES AND COLLISION LIFETIMES

Gas	θ , sec	θ_1 , sec	R , sec ⁻¹	Z_{10}	ν_1 , cm ⁻¹	$\nu_1^{2/3} M^{1/3}$
CH ₃ Br	$7.5 \pm 0.3 \times 10^{-8}$	$3.4 \pm 0.1 \times 10^{-8}$	$10.79 \pm 0.22 \times 10^9$	386 ± 14	611	328
CHClF ₂	9.5 ± 0.7	2.3 ± 0.2	9.98 ± 0.20	268 ± 24	369	227
CH ₃ Cl	20.4 ± 1.1	8.6 ± 0.5	10.91 ± 0.22	966 ± 67	732	300
CCl ₃ F	4.0 ± 0.4	1.5 ± 0.2	11.79 ± 0.24	234 ± 31	244	202
CBrClF ₂	5.0 ± 0.4	$.9 \pm 0.1$	9.66 ± 0.48	121 ± 15	200	188
CF ₄	75.6 ± 0.8	32.1 ± 0.3	6.84 ± 0.34	$2,460 \pm 125$	437	256
CH ₂ F ₂	3.0 ± 0.3	1.5 ± 0.2	9.81 ± 0.49	159 ± 24	332	245
CH ₂ ClF	1.0 ± 0.1	$.45 \pm 0.05$	11.20 ± 0.56	60 ± 7	358	206
CClF ₃	23.9 ± 0.6	9.3 ± 0.2	11.28 ± 0.23	$1,240 \pm 37$	356	237
CHCl ₂ F	2.5 ± 0.4	$.6 \pm 0.1$	11.48 ± 0.57	89 ± 15	274	198
CHF ₃	47.9 ± 1.8	24.9 ± 0.9	8.34 ± 0.42	$2,260 \pm 140$	308	263
CCl ₂ F ₂	7.8 ± 0.6	1.6 ± 0.1	10.31 ± 0.21	212 ± 14	260	201
CBr ₂ F ₂	2.9 ± 0.3	$.50 \pm 0.05$	9.34 ± 0.47	68 ± 8	165	179
CBrF ₃	19.6 ± 0.1	8.4 ± 0.1	8.05 ± 0.40	840 ± 43	297	239

TABLE III

DATA OF OTHER INVESTIGATORS

Gas (a)	Investigator	T, °K	θ , sec	Z_{10}	Z_{10} at T = 300° K	ν_1 , cm ⁻¹	$\nu_1^{2/3} M^{1/3}$
CH ₃ I	Fogg, Hanks, and Lambert (ref. 12)	373	4.5×10^{-8}	86	176	333	342
CHCl ₃	Fogg, Hanks, and Lambert (ref. 12)	383	2.8	83	139	260	200
CH ₂ Cl ₂	Fogg, Hanks, and Lambert (ref. 12)	373	8.4	204	466	283	192
CH ₃ F	Fogg, Hanks, and Lambert (ref. 12)	373	320	6,070	29,400	1,048	336
CCl ₄	Fogg, Hanks, and Lambert (ref. 12)	373	8.3	191	348	218	197
CH ₃ Br	Fogg, Hanks, and Lambert (ref. 12)	373	10	202	468	611	328
CH ₂ F ₂	Fogg, Hanks, and Lambert (ref. 12)	373	5.5	136	278	532	248
CHF ₃	Fogg, Hanks, and Lambert (ref. 12)	373	42	1,200	3,720	508	263
CH ₃ Cl	Fogg, Hanks, and Lambert (ref. 12) Griffith (ref. 17) Petrálie (ref. 16)	373 295 287	18 20.2 20.2	424 956 956	1,200	732	300
CF ₄	Fogg, Hanks, and Lambert (ref. 12) Byers (ref. 14)	373 293	66 76	1,580 2,480	6,210	437	256
CH ₄	Eucken and Aybar (ref. 15)	382	84	6,000	36,000	1,306	302
CCl ₂ F ₂	Huber and Kantrowitz (ref. 18) Griffith (ref. 17)	297 292	2 8	49 218		260	201
CHClF ₂	Griffith (ref. 17)	294	10	282		369	227

^aCH₃I, methyl iodide; CHCl₃, trichloromethane; CH₂Cl₂, dichloromethane; CH₃F, fluoromethane; CCl₄, tetrachloromethane; CH₄, methane; other compounds identified in text.

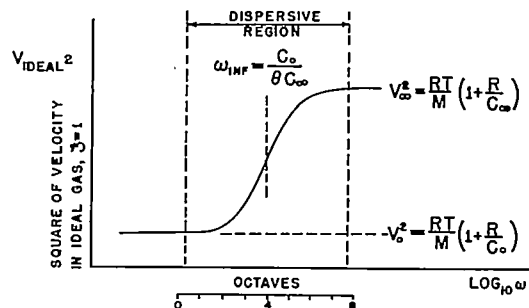


Figure 1.- Sonic velocity versus frequency for thermal relaxation process.

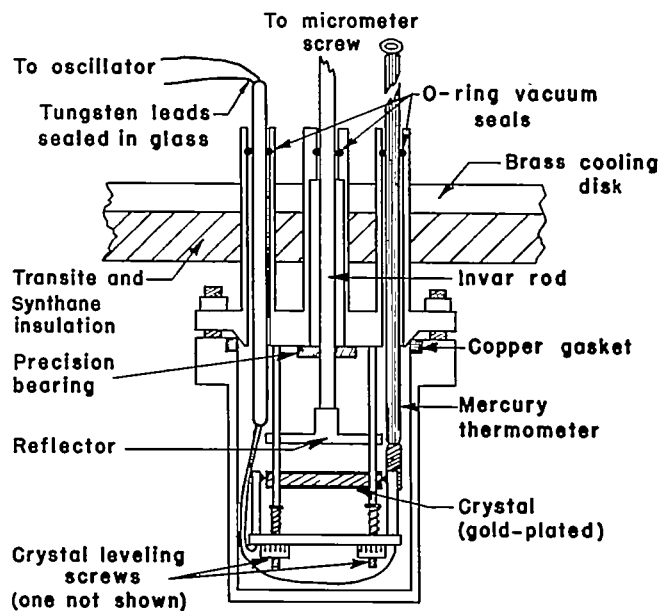


Figure 2.- Interferometer cup showing crystal mounting.

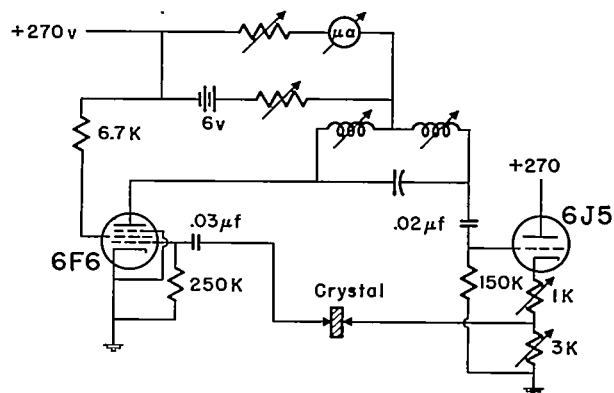


Figure 3.- Crystal oscillator circuit.

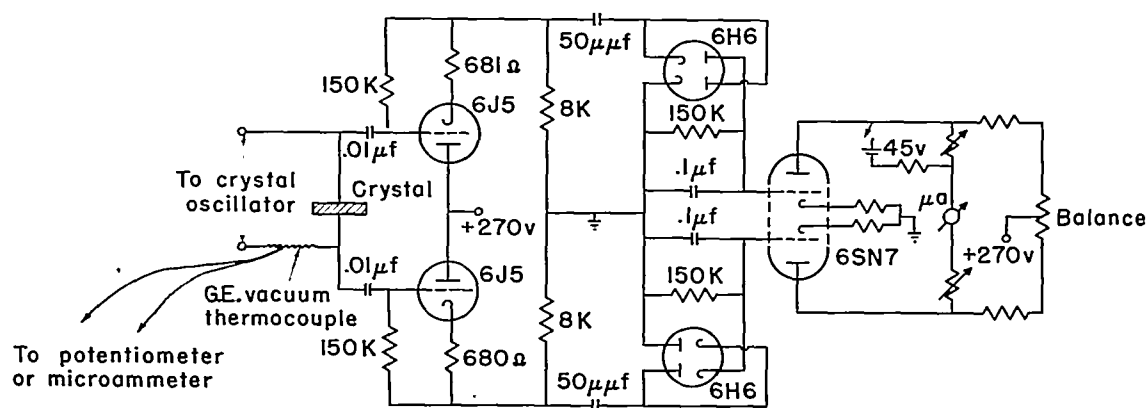


Figure 4.- Crystal impedance-measuring circuit.

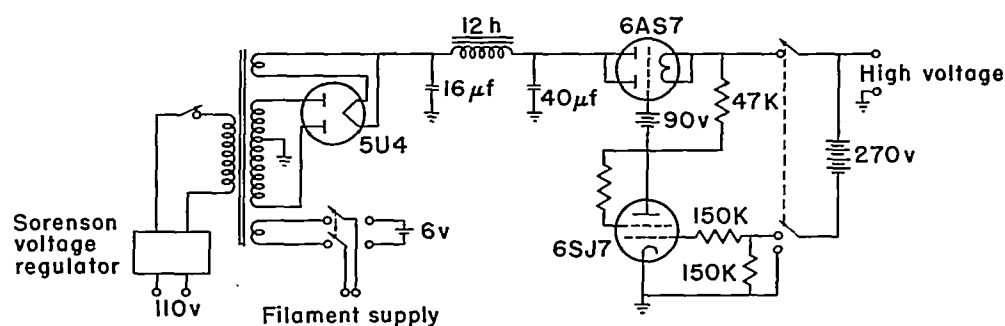


Figure 5.- Power supply with voltage regulator.

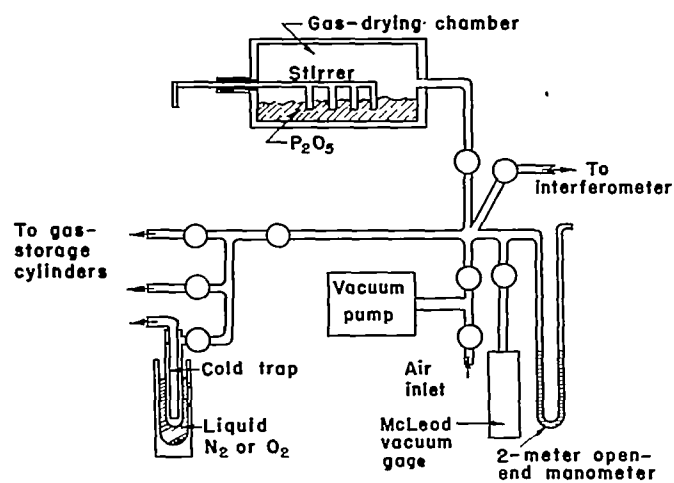
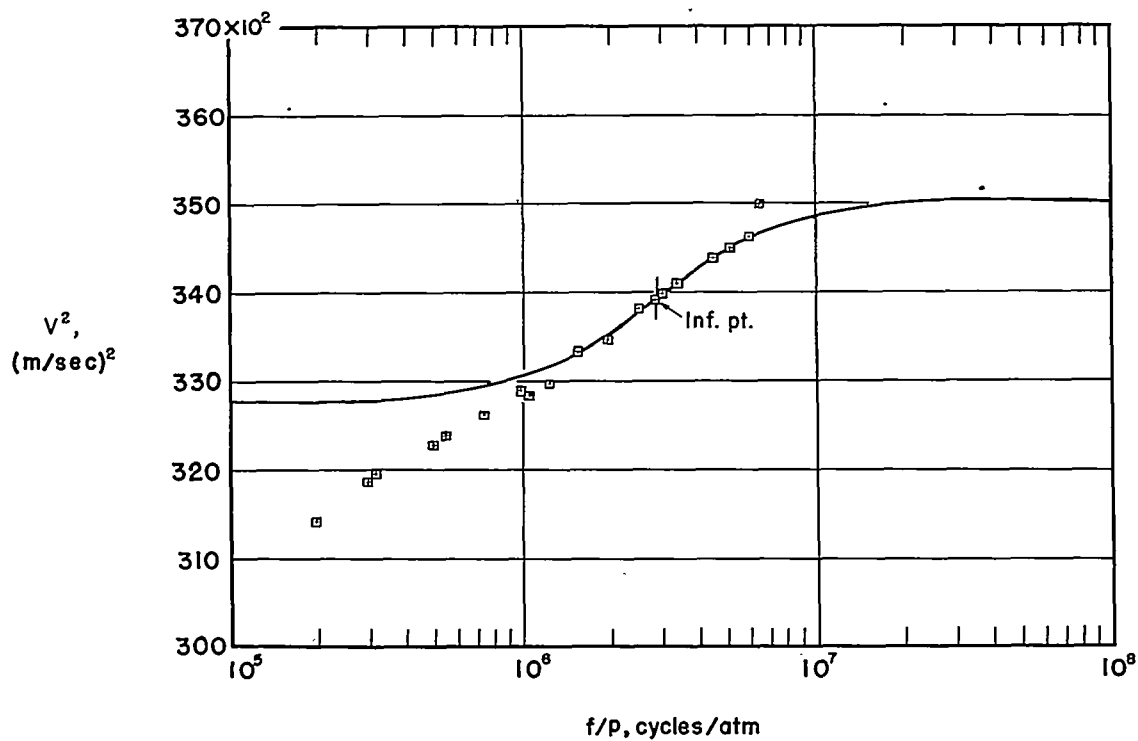
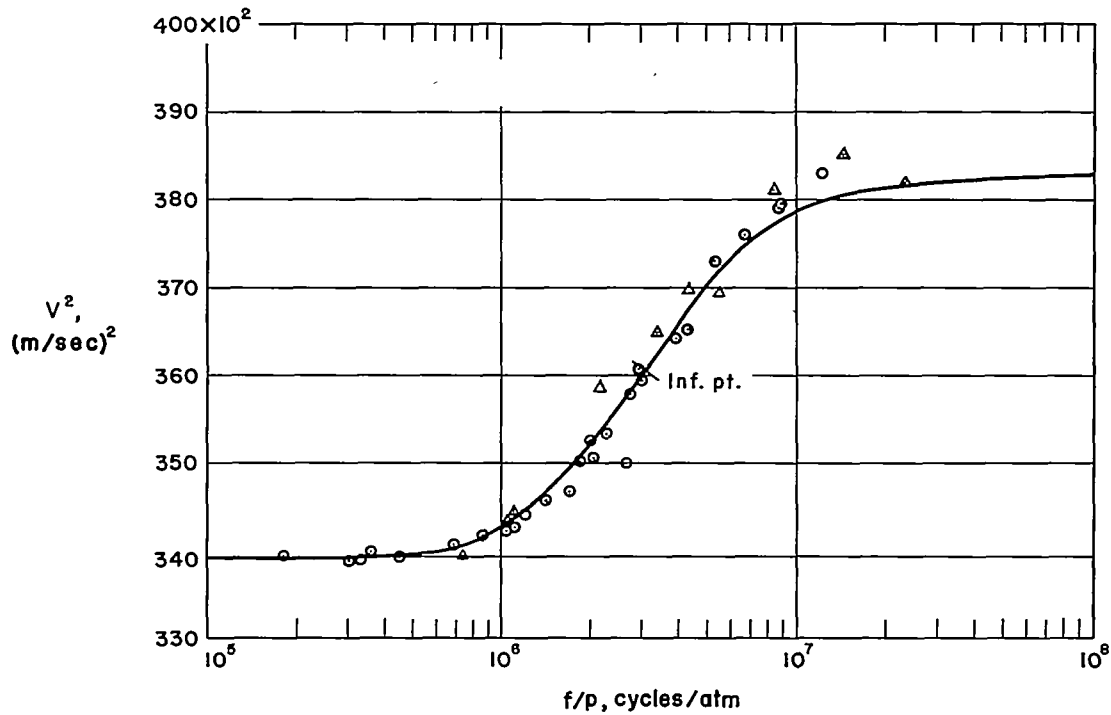
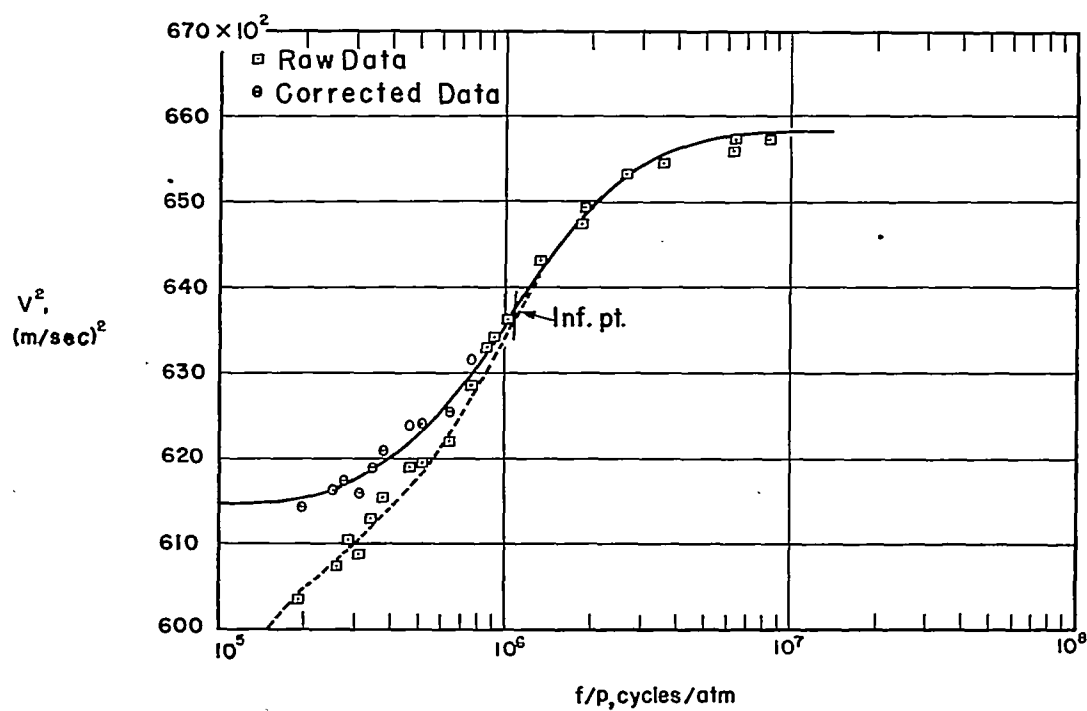
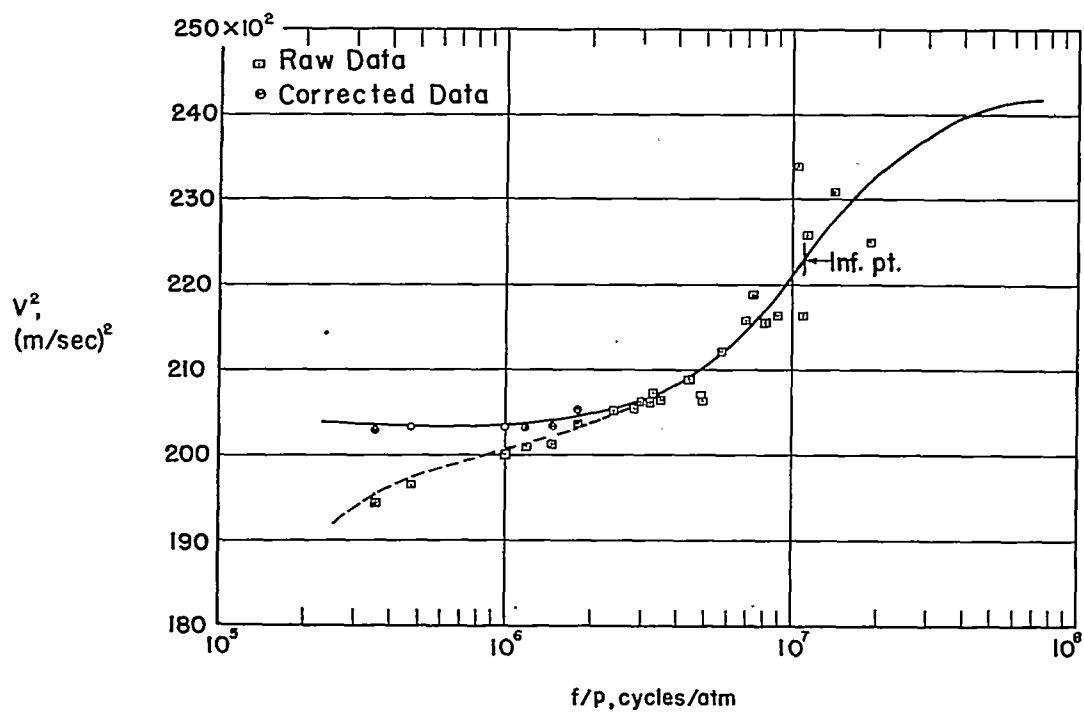
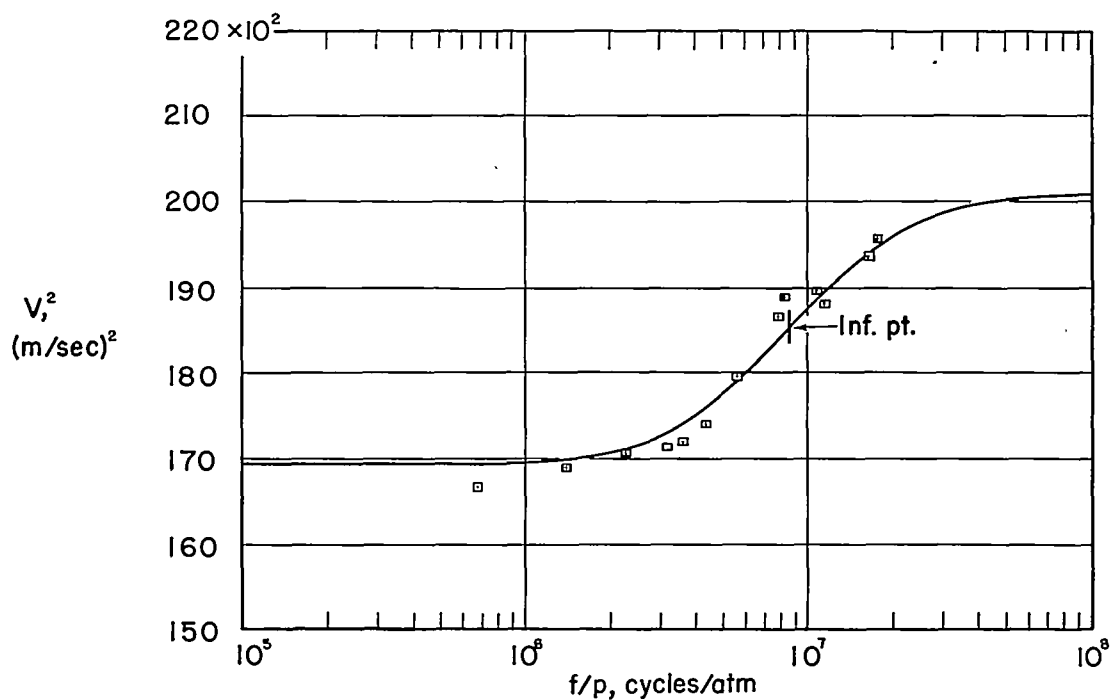
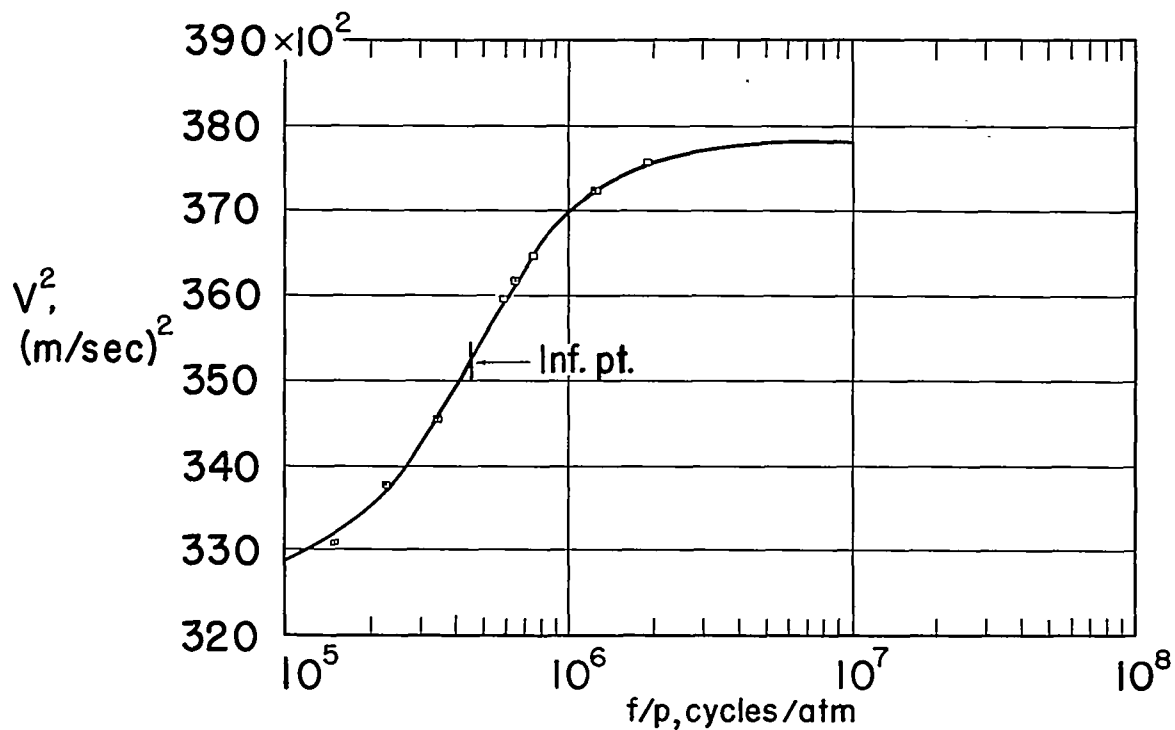
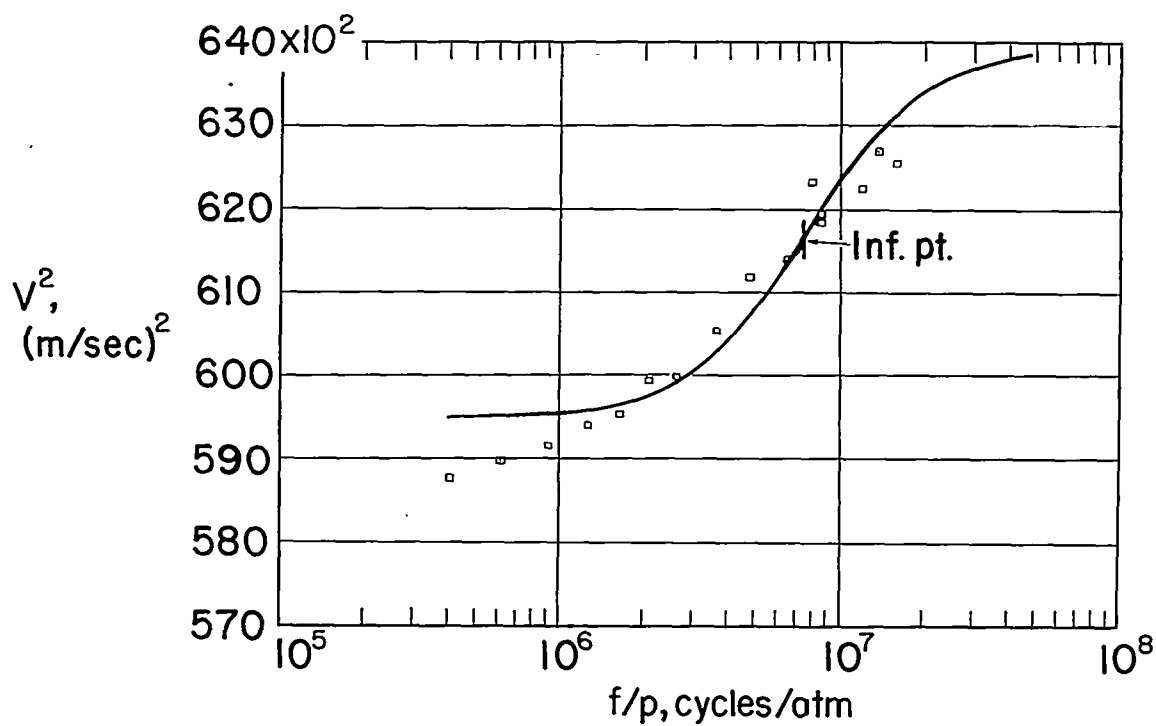
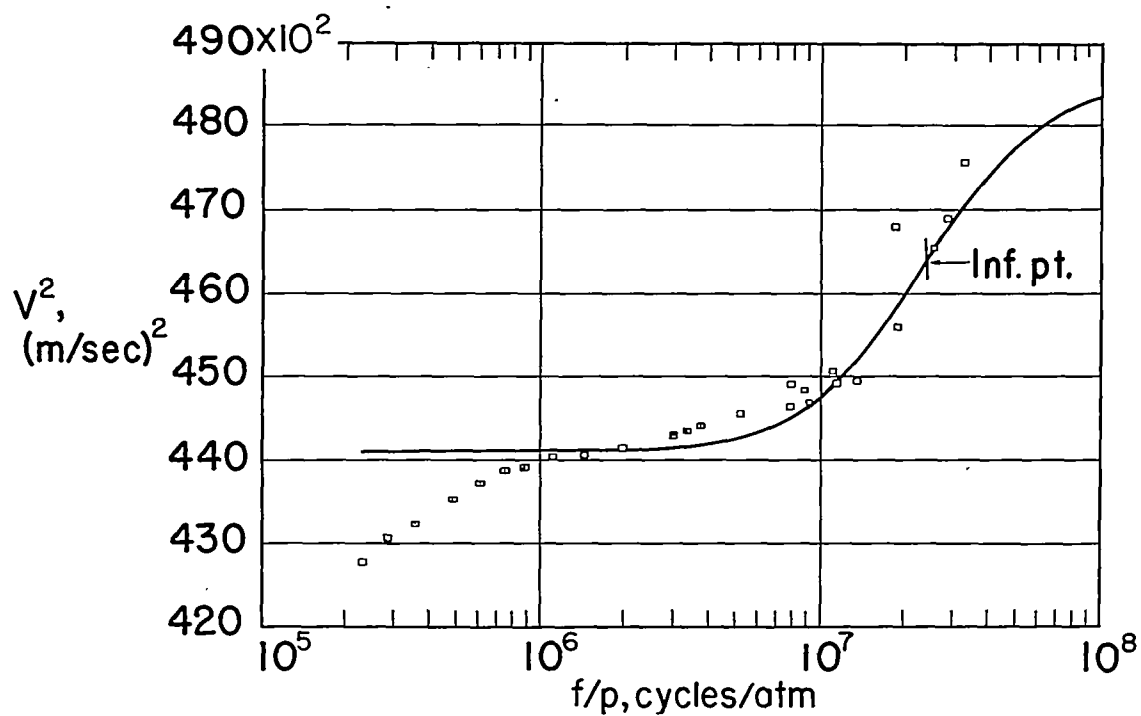


Figure 6.- Gas-handling and vacuum equipment.

Figure 7.- Velocity dispersion in CH_3Br .Figure 8.- Velocity dispersion in CHClF_2 .

Figure 9.- Velocity dispersion in CH_3Cl .Figure 10.- Velocity dispersion in CCl_3F .

Figure 11.- Velocity dispersion in CBrClF_2 .Figure 12.- Velocity dispersion in CF_4 .

Figure 13.- Velocity dispersion in CH_2F_2 .Figure 14.- Velocity dispersion in CH_2ClF .

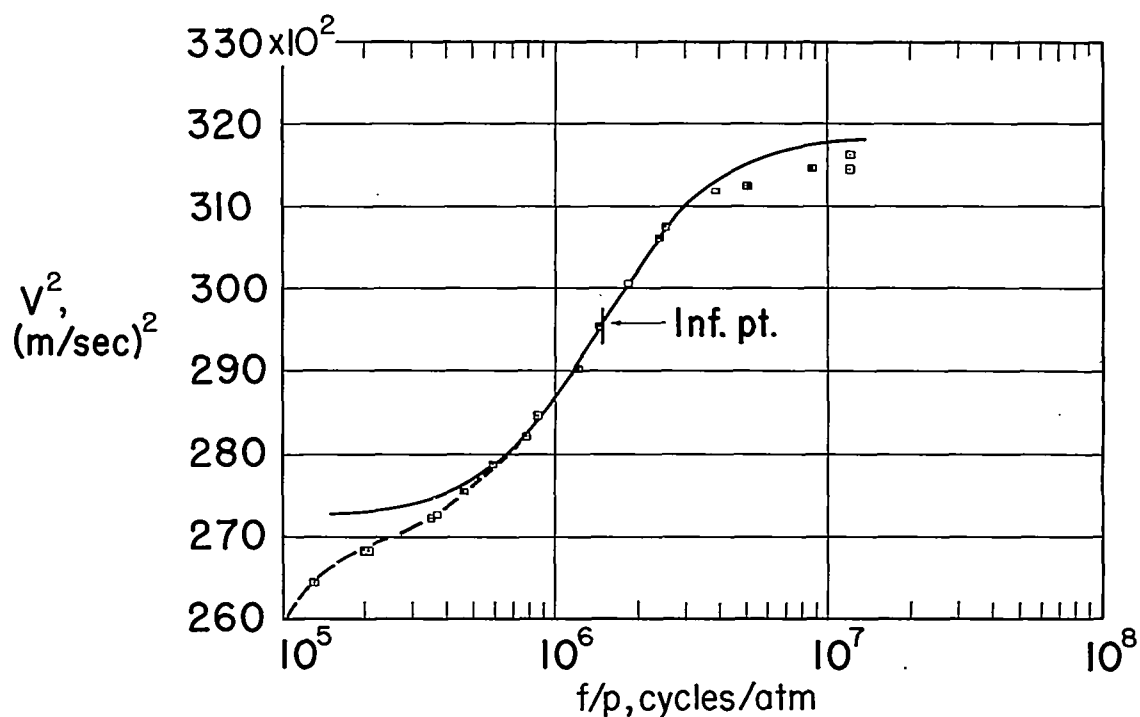


Figure 15.- Velocity dispersion in CClF_3 .

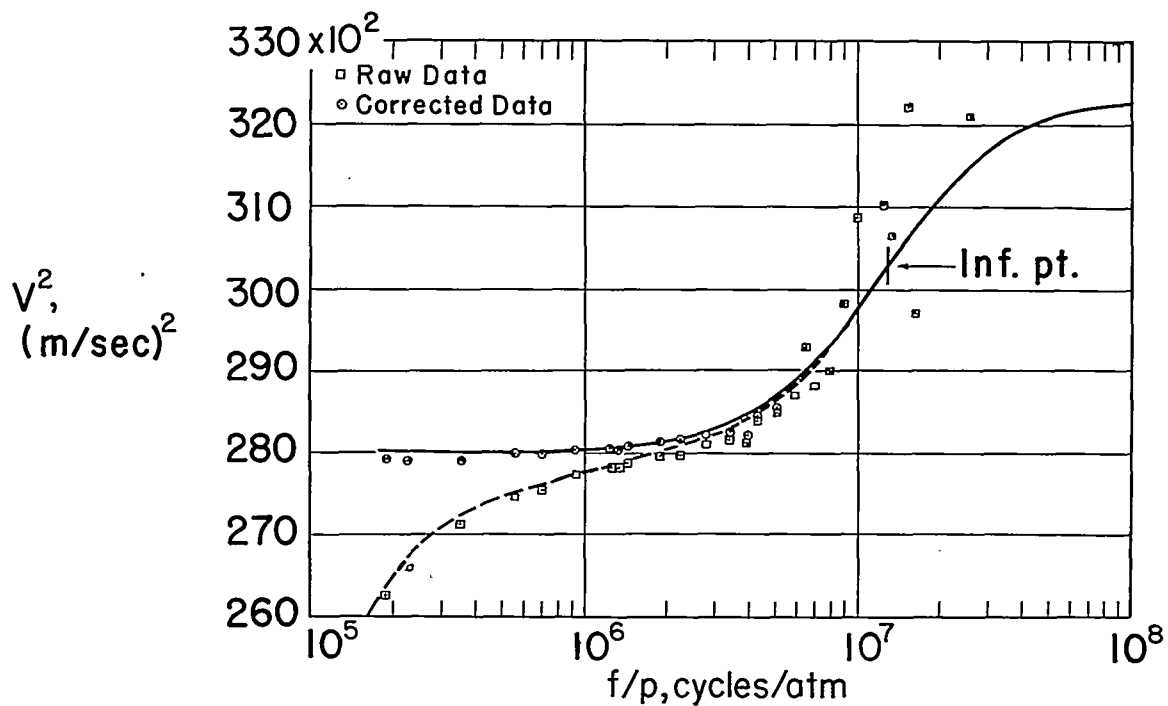
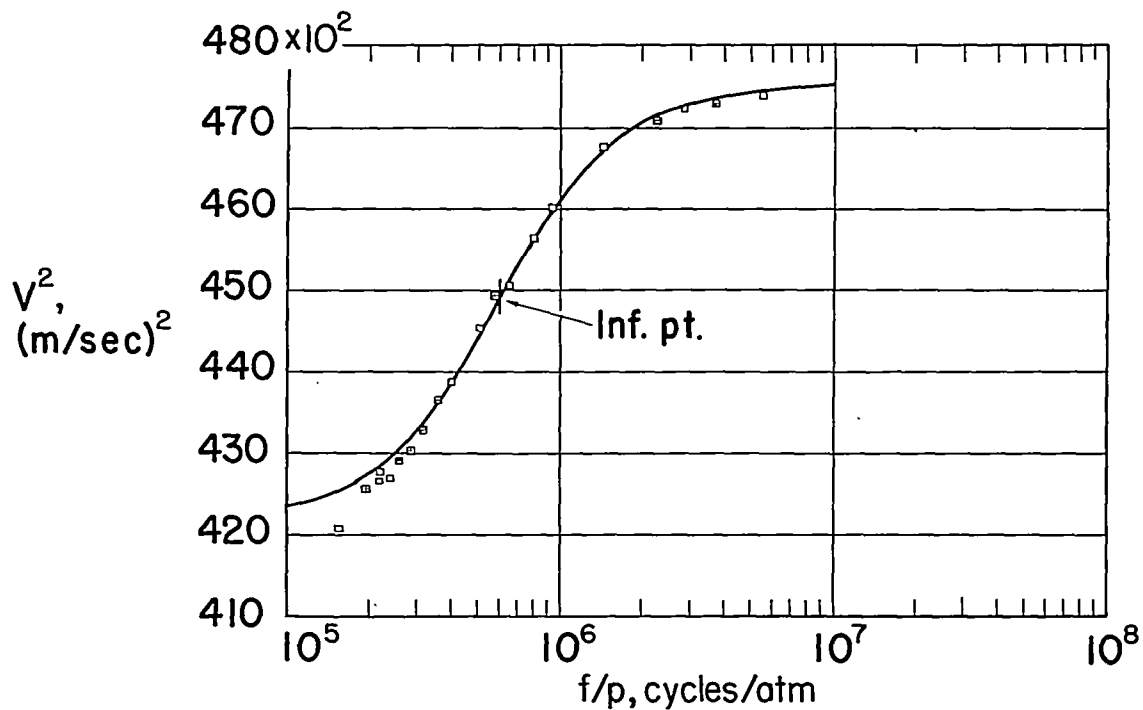
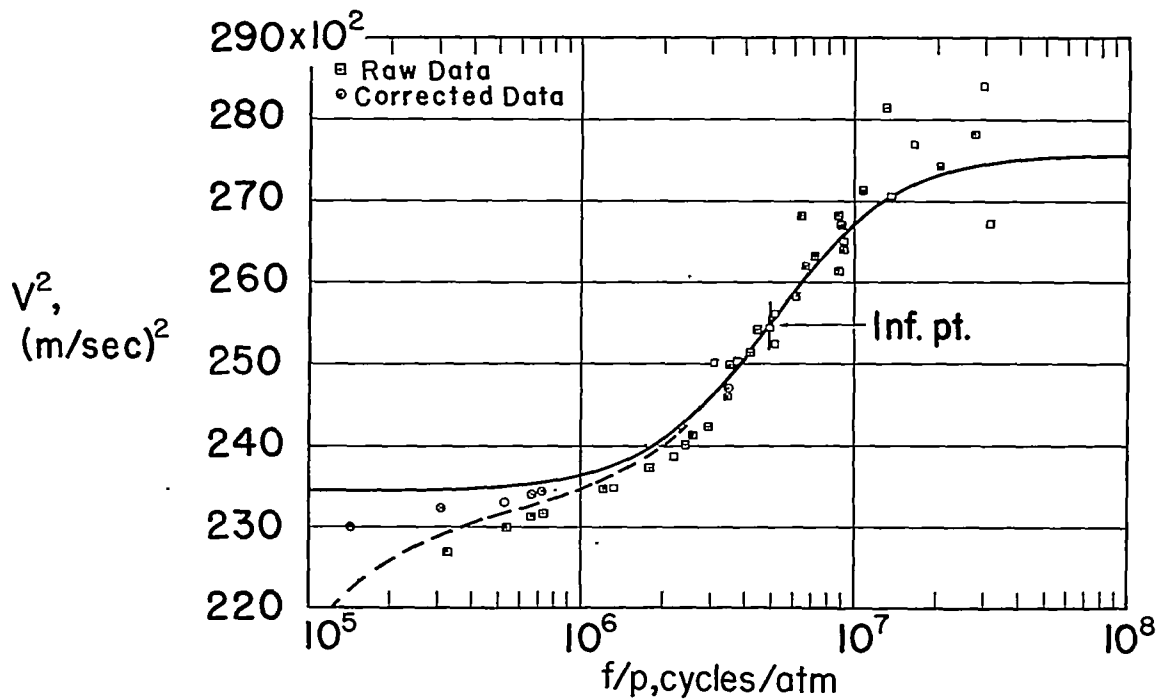
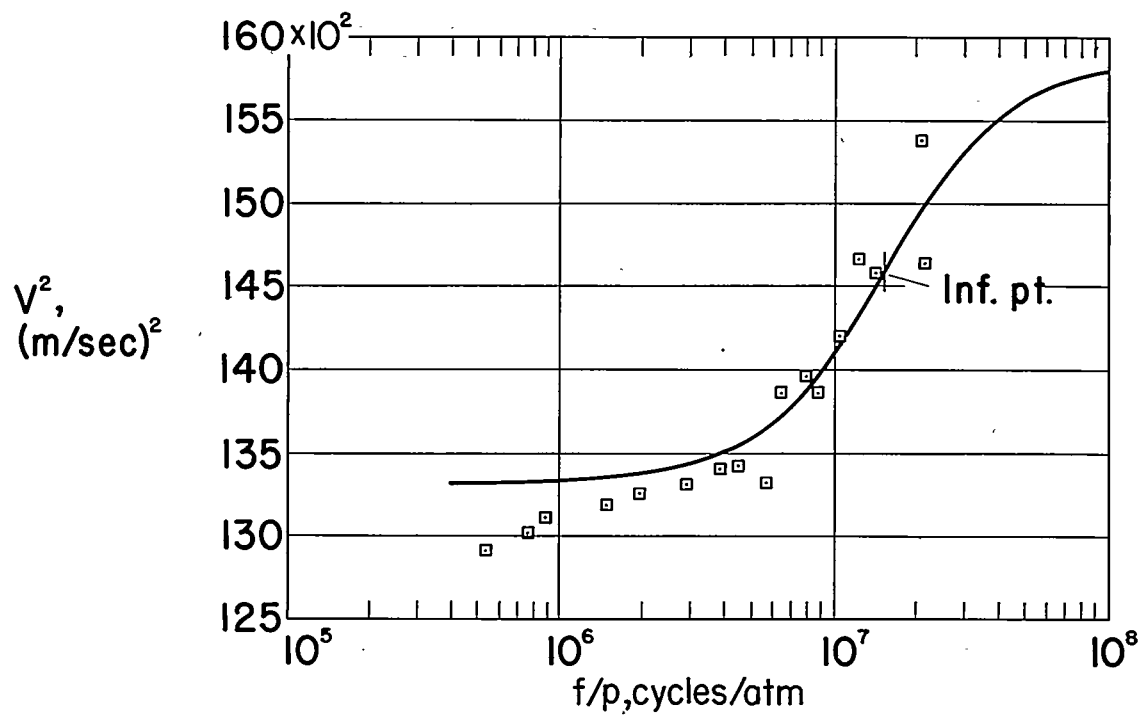
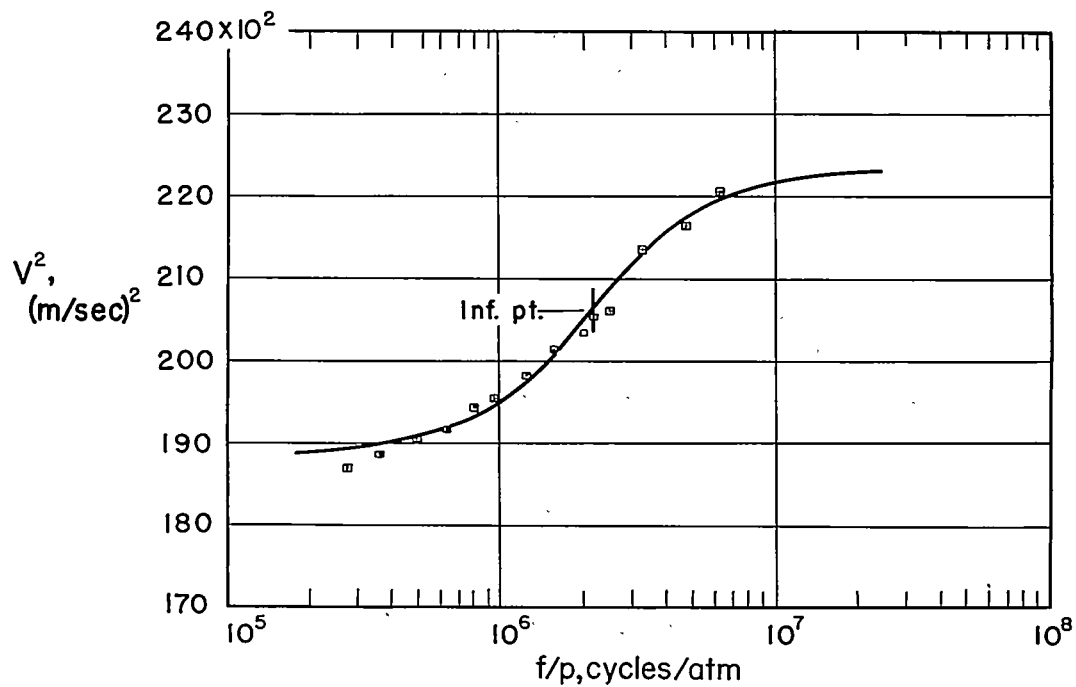


Figure 16.- Velocity dispersion in CHCl_2F .

Figure 17.- Velocity dispersion in CHF_3 .Figure 18.- Velocity dispersion in CCl_2F_2 .

Figure 19.- Velocity dispersion in CBr_2F_2 .Figure 20.- Velocity dispersion in CBrF_3 .

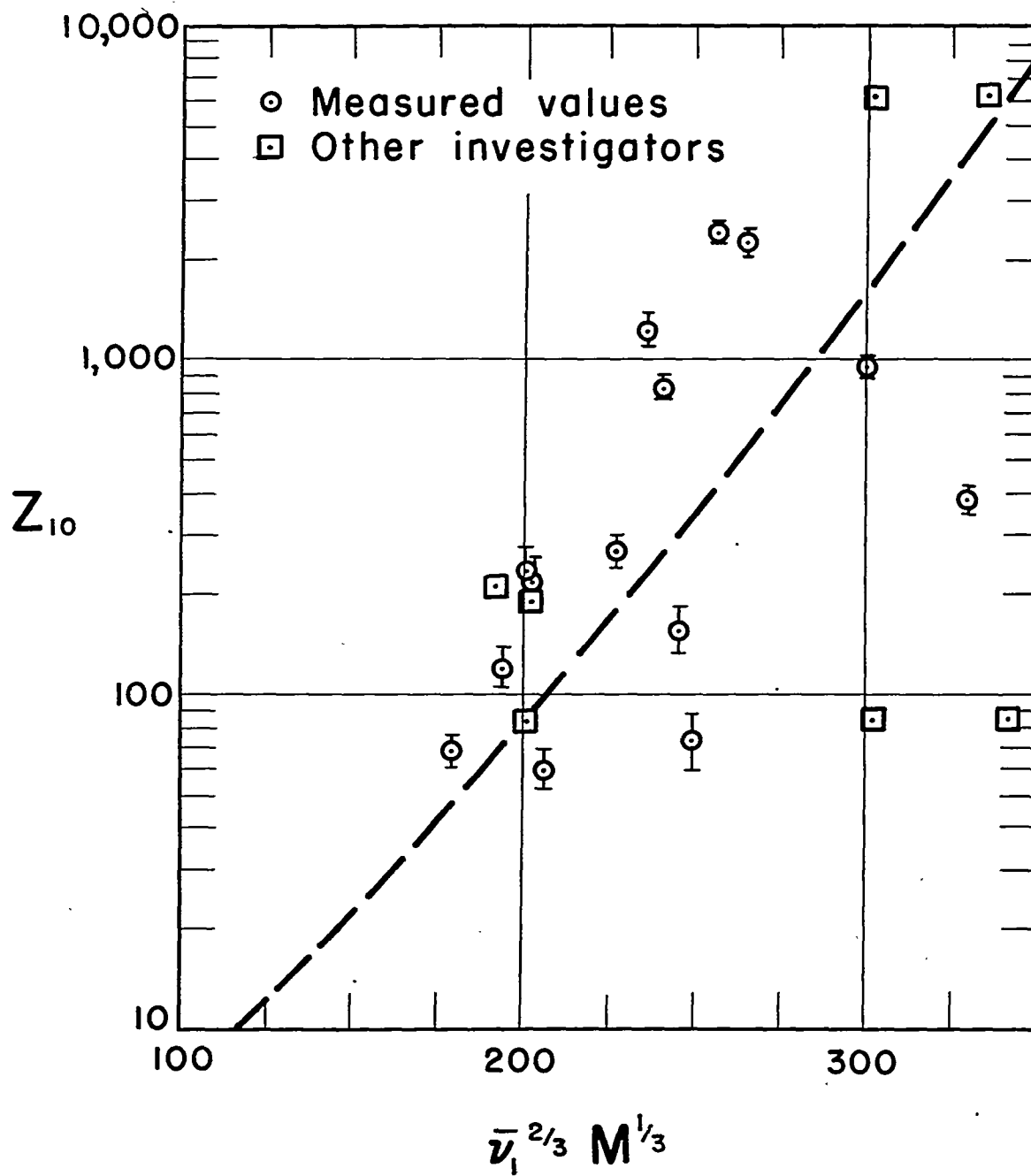


Figure 21.- Z_{10} interpreted by Landau-Teller theory. $\alpha = 0.5$; $s = 0.25A$.

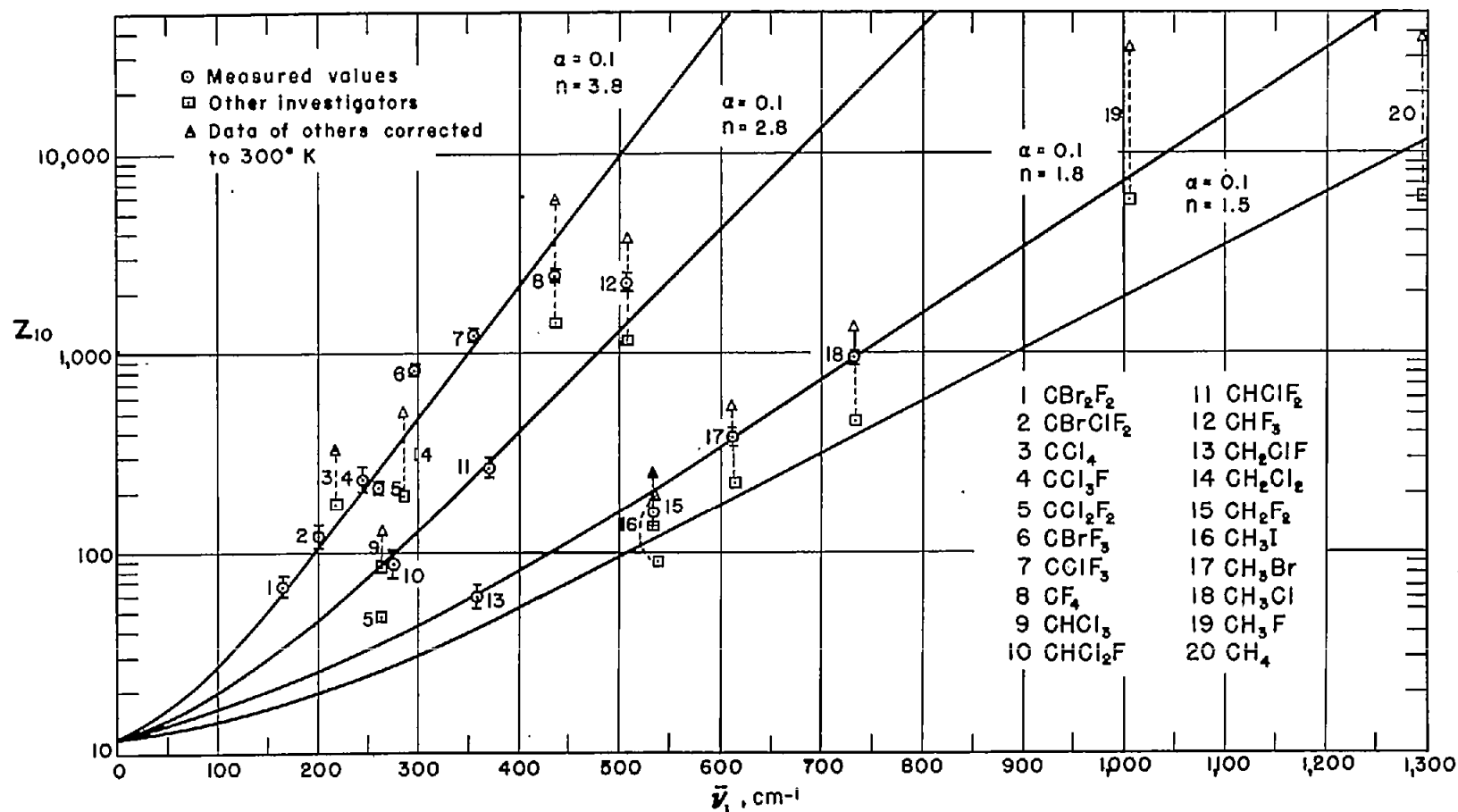


Figure 22.- Z_{10} interpreted by energy-excitation theory.